

RECENT STUDIES ON METHANOL CROSSOVER IN LIQUID-FEED DIRECT METHANOL FUEL CELLS

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Abstract

In this work, the effects of methanol crossover and airflow rates on the cathode potential of an operating direct methanol fuel cell are explored. Techniques for quantifying methanol crossover in a fuel cell and for separating the electrical performance of each electrode in a fuel cell are discussed. The effect of methanol concentration on cathode potential has been determined to be significant. The cathode is found to be mass transfer limited when operating on low flow rate air and high concentrations of methanol. Improvements in cathode structure and operation at low methanol concentration have been shown to result in improved cell performance.

Introduction

Since the early 90's the Jet Propulsion Laboratory has been pursuing the development of direct methanol fuel cells (DMFCs) under DARPA sponsored programs [1, 2]. The DMFC operates by oxidizing an aqueous solution of methanol to CO_2 and reducing oxygen, from an air stream, to water. The heart of a DMFC is the membrane-electrode assembly (MEA) and it is typically composed of three major components: a Pt-Ru anode, a Pt cathode, and a proton exchange membrane (PEM). Research on DMFCs is currently being pursued at several institutes in the United States and abroad, and various processes in such fuel cells have been investigated [2, 5-6].

The simplicity of the liquid feed direct methanol fuel cell arises from ease of membrane hydration and practical portability of fuel cell reactants. As in all PEM type fuel cells, membrane hydration level is the key to the electrochemical performance of the fuel cell [4]. The ease of membrane hydration allows for the DMFC to be operated over a wide range of environmental conditions. The current state of technology for direct methanol fuel cells is 0.470 V at an applied current density of 150 mA/cm^2 for a cell running at 60°C , and 5L/min ambient airflow [3].

Under a DARPA-sponsored effort, JPL is currently developing a 150-watt DMFC power source for DOD applications. For this application the fuel cell system must be lightweight and capable of operating over a wide range of environmental conditions. The understanding and characterization of the effects of methanol crossover on a DMFC are crucial to the design of practical portable power systems. The following focuses on the electrochemical evaluation of MEAs for implementation in a DARPA 150-watt power source. The study specifically relates to the measurement of methanol crossover rates, evaluation of anode and cathode performance and identification of optimal conditions for fuel cell operation.

Experimental

The MEAs analyzed in this study incorporated an in-house developed process, which allows for the direct deposit of catalyst to a dry Nafion® membrane by various techniques such as spraying, painting, or pouring of the catalyst ink. Both MEAs tested were constructed with the following catalyst loading. The anode and cathode catalyst loading on to the membrane was 4 mg/cm^2 each. Two carbon papers of 25 cm^2 area were coated with Pt and Pt-Ru to make up the current collectors for the cathode and anode respectively. The total catalyst loading is estimated to be between $8\text{-}12 \text{ mg/cm}^2$.

The MEAs are first conditioned at 90°C , 1M methanol, 5 L/min airflow at 20 psig. This step is done to hydrate the MEA and to activate the proton conducting ionomer in the catalyst layer. The high current densities that can be achieved under these testing conditions are required to ensure optimal DMFC performance. MEA characterization is carried out at molarities ranging from 0.25 to 1.5M, with airflow rates ranging from 0.1 to 5 L/min, and temperatures ranging from 20 to 90°C . Crossover experiments are performed using oxygen as the oxidant. The cathode exhaust gases are then passed through a CO_2 analyzer, which determines the CO_2 volume percent in the exit gas [3]. The final experiments are to determine the electrical performance contributions coming from the cathode and anode separately. To separate the electrode performance it is necessary to introduce hydrogen into the cathode feed of the fuel cells. In this case, the cathode becomes a dynamic hydrogen reference electrode. These test are performed last so that any side effects on the cathode caused by the introduction of hydrogen would not show up in the characterization at the cell level.

Results

Figures 1, 2 and 3 are for crossover experiments performed with methanol concentration of 0.5, 1.0, and 1.5M respectively. In comparing the charts one can ascertain the impact of temperature on the effective crossover current density for a given operating concentration of methanol. At fixed current density of 100 mA/cm^2 , the effective methanol crossover rate increases from 35 to 137 mA/cm^2 as the methanol molarity increases from 0.5M to 1.5M at 60°C .

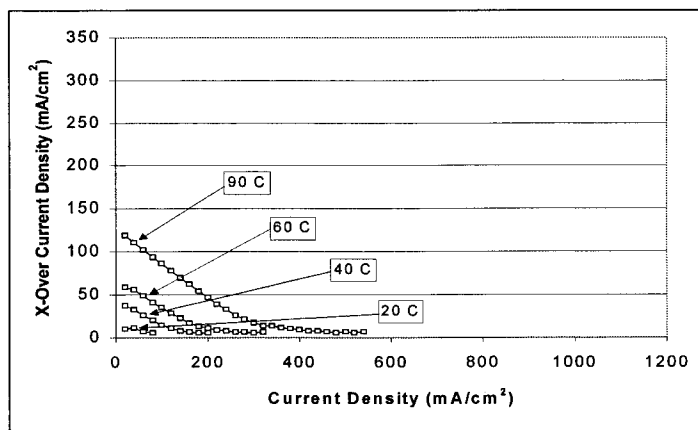


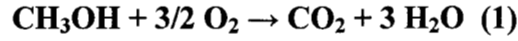
Figure 1. The effects of increasing temperature on crossover rate for a DMFC operating at 0.5M methanol.

Methodology

The performance of DMFCs is characterized by evaluation of methanol crossover, anode and cathode polarization. The processes and the techniques used in understanding them are described as follows.

Methanol Crossover

The crossover reaction at the cathode is given as equation (1).



The CO₂ content of the cathode stream is measured using a Horiba VIA 550 gas analyzer. A volume flow rate of CO₂ can then be determined by multiplying the oxidant flow rate by the vol% of CO₂ read from the gas analyzer. Using the ideal gas law this volume can be converted to a flow rate of moles of CO₂/ sec. Faraday's law can now be used to calculate an equivalent current. If n represents the number of moles of CO₂ produced per second,

$$I = nFn_e \quad (2)$$

Where F is Faraday's constant, and n_e is the number of electrons involved in the reaction. This equivalent current can then be normalized for the electrode area to get an effective crossover current density. This measurement of crossover can be carried out during fuel cell operation and also as a function of the applied load.

Anode and Cathode Polarization

Anode polarization experiments refer to an experiment when hydrogen is introduced into the cathode compartment so as to allow it to behave as a dynamic hydrogen electrode. Under these conditions, the resultant polarization curve will be that of E_a vs. applied current density. After correcting for resistance losses, E_a can now be algebraically added to the cell potential vs. applied current density curve to determine the cathode potential, E_c as such:

$$E_c = E_{\text{cell}} + E_a \quad (3)$$

In this way one can determine the relative contributions to electrical performance resulting from the anode or the cathode. These polarization results can be combined with crossover rate measurements to determine the effects of crossover on E_c .

The cathode has to provide for both the electrochemical oxidation of the methanol crossing over as well as for the O₂ reduction reaction. In this sense, polarization at the cathode is effectively caused by the applied current density and the crossover current density. The total applied current density is given as equation 4.

$$I_{\text{tot}} = I_{\text{app}} + I_{\text{cross}} \quad (4)$$

When E_c is plotted against this total current density, the true polarization behavior of the cathode can be obtained.

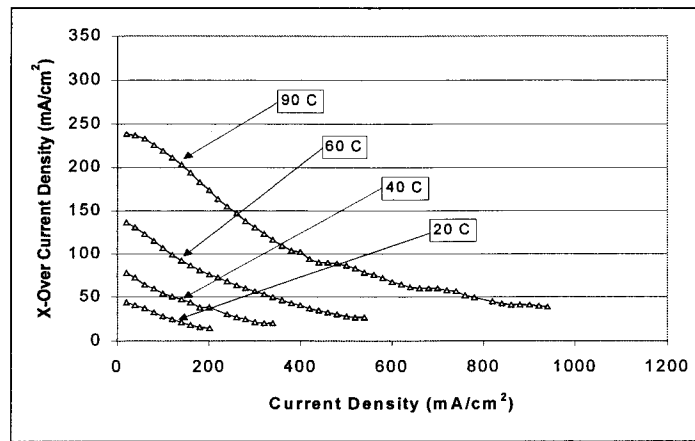


Figure 2. The effects of increasing temperature on crossover rate for a DMFC operating at 0.5M methanol.

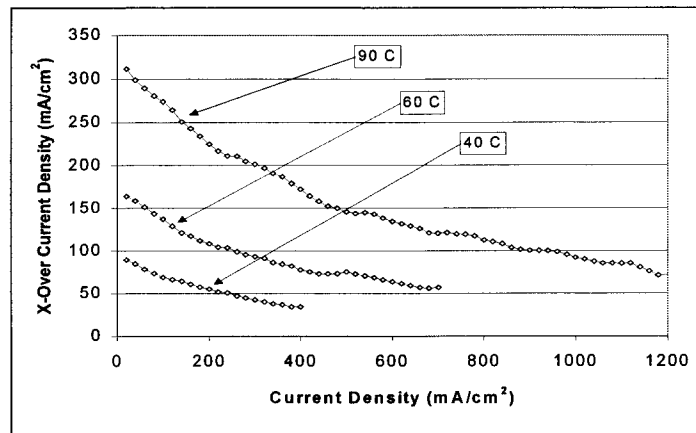


Figure 3. The effects of increasing temperature on crossover rate for a DMFC operating at 0.5M methanol.

The effect of methanol molarity and airflow rate on a DMFC are shown in Figure 4. As the methanol concentration decreases, cell voltages can increase by as much as 50 mV at current densities of 100 mA/cm². In Figure 4, the cell voltage is shown as 0.362 V at 100 mA/cm², for a cell operating with 60°C, 1M methanol and 0.1 L/min of ambient pressure airflow. With the reduced methanol concentration of 0.5M, the cell voltages for 60°C, and 0.1 L/min ambient airflow rate operation are 0.419 V. The calculated air stoichiometry at a 100 mA/cm² for 0.1 L/min, 0.5M methanol corresponds to 1.7 times stoic when the air required to oxidize the methanol that crosses over is also included. A similar increase in DMFC performance can be seen when one increases the airflow rate. At 0.3L/min, the cell voltage is 0.403 V for 60 °C, 1M methanol. The calculated air stoichiometry at a 100 mA/cm² for 0.3 L/min, 1.0M methanol corresponds to 3.35 times stoic.

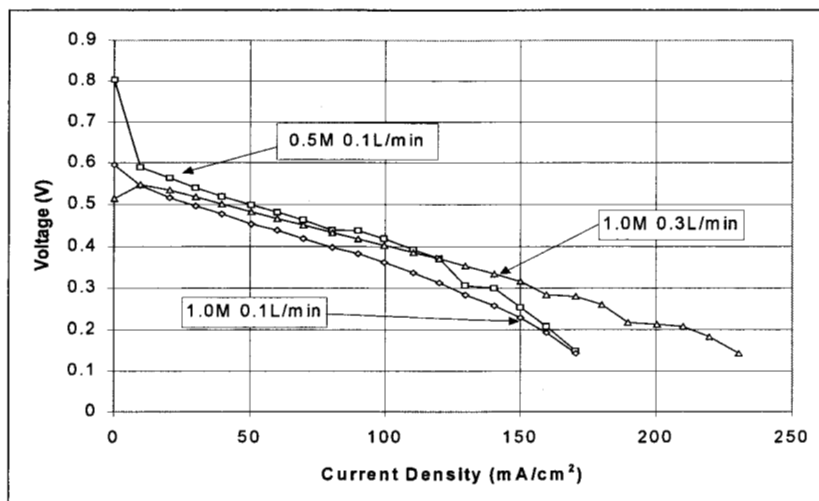


Figure 4. The effect of molarity and ambient airflow rate on the electrochemical performance of a DMFC at 60 °C.

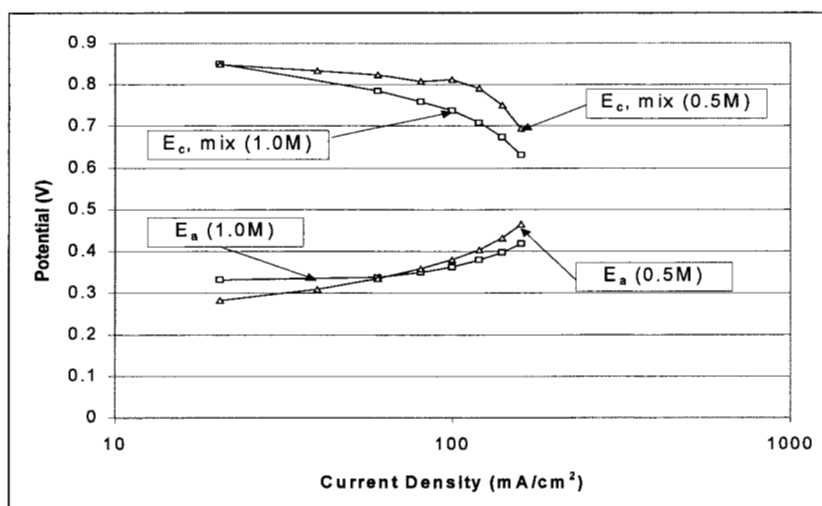


Figure 5. The effect of methanol concentration on the electrochemical performance of the anode and cathode in a DMFC operating at 60 °C, 0.1 L/min ambient airflow rate.

The effect of methanol concentration on the electrochemical performance for both the anode and cathode are shown as a function of current density in Figure 5. The polarization losses at the anode are minimal and there is a marginal improvement in performance of the anode on increasing the concentration from 0.5 to 1.0M at current density of 120 mA/cm². The cathode polarization plot obtained is a plot of the mixed potential, $E_{c, mix}$, because of the effects of methanol crossover on that electrode. Increasing the methanol concentration lowers the cathode potential to the extent of 50-100 mV.

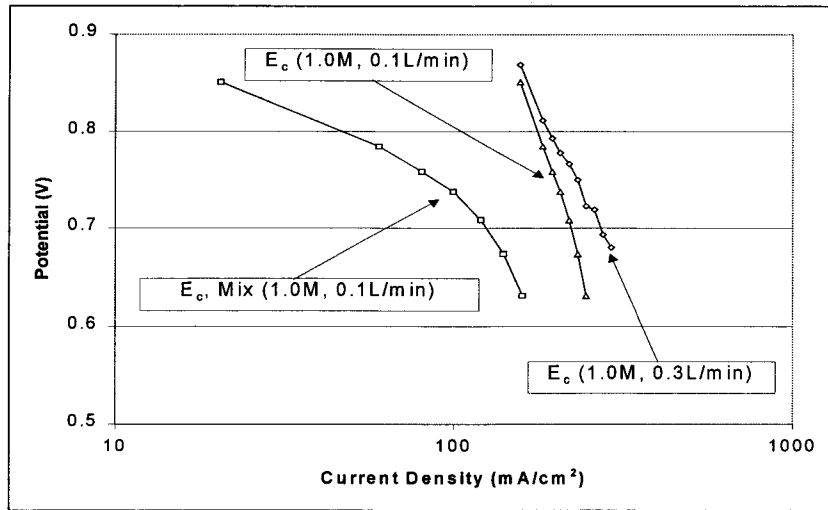


Figure 6. The effects of methanol crossover on the cathode of a fuel cell operating at 1.0M methanol.

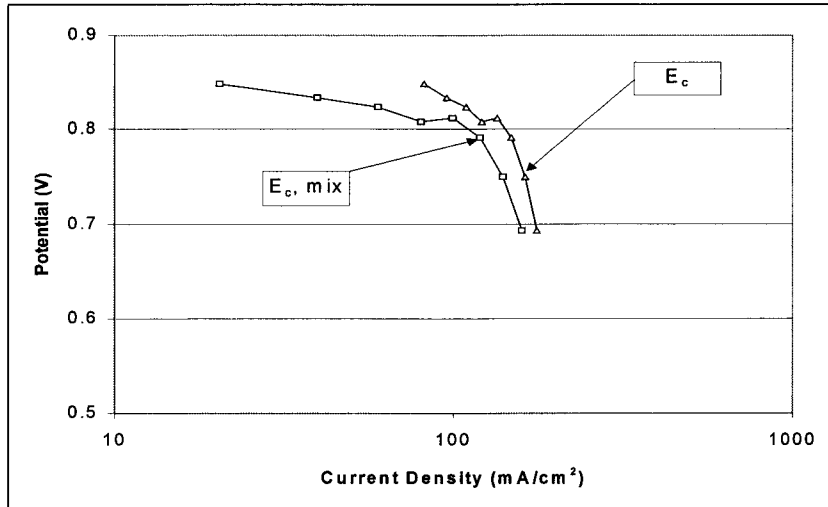


Figure 7. The effects of methanol crossover on the cathode of a fuel cell operating at 0.5M methanol.

The effects of methanol crossover on the cathode potential, $E_{c,mix}$, as a function of applied current density can be seen in Figures 6 and 7. The true cathode potential, E_c , can be determined when one includes the air demand due to crossover as per equation (4). In Figure 6, the 1M methanol case, E_c is always in a mass transfer limited regime regardless of airflow rate. When the methanol molarity is reduced to 0.5M, the overall performance of the cathode is improved as shown in Figure 7. The true cathode potential becomes mass transfer limited only at current densities upwards of 130 mA/cm² operating on 0.5M methanol.

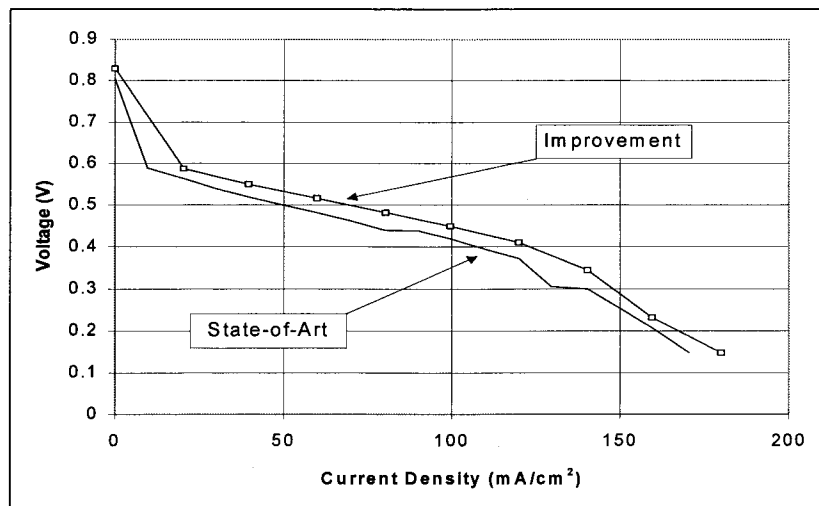


Figure 8. The effect of cathode structure for a DMFC operating at 60 °C, 0.5M methanol, and 0.1 L/min ambient airflow.

Thus it is important to reduce the mass transfer barriers at the cathode, and results of such improvements are shown in Figure 8. At an applied current density of 100 mA/cm² a 30 mV improvement can be attained with an improved cathode catalyst structure. Cell voltages of 0.449 V at 100 mA/cm² are shown for a DMFC operating at 60 °C, 0.5M methanol, and 0.1 L/min of ambient airflow. Under the same conditions the cell is able to perform at voltage as high as 0.410 V at current densities of 120 mA/cm². The air stoichiometry at 120 mA/cm² corresponds to 1.55 times stoic, when the air required to oxidize the methanol that crosses over to the cathode is included.

Discussion

It has been observed that higher operating voltages at current densities below 150 mA/cm² can be obtained when a lower concentration of methanol is used in the operation of a DMFC. A possible reason for this is that the effective crossover rate is less at lower concentrations. The cathode is affected in two ways by crossover; the water produced from the crossover reaction can form a physical barrier to O₂ permeation at the cathode catalyst membrane interface, and the methanol crossing over places an additional demand on the oxygen available at the cathode. When more oxygen is introduced to the cell, in the form of an increased airflow rate, the cell performance is improved. The difference between the 0.1 L/min, 0.5M methanol and 0.3 L/min 1.0M methanol at 60 °C is 16 mV at 100 mA/cm² which states that equivalent performances can be obtained under two different operating conditions. The problem is that when one views DMFC performance in light of a total system, the increase from 0.1 to 0.3 liter/min airflow operation translates into increased system weight and complexity.

The results in Figures 1 and 2 demonstrate that methanol molarity has an effect on cell performance. At 1M methanol, the cathode is essentially always mass transfer limited. Even when the airflow rate is tripled, there are significant mass transfer limitations at the cathode. Thus, at 60 °C, the crossover resulting from 1M methanol overwhelms the electrode in such a manner that even increasing the amount of O₂ to the cathode does not

make available more O₂ for the reaction. On the other hand, reducing the methanol concentration has the greatest impact on cell performance at 60 °C and at airflow rates less than 2 times stoichiometric. E_c, in the 0.5M case in Figure 7, shows a distinct kinetic region for current densities as high as 120 mA/cm².

Conclusions

It has been determined that methanol concentration has a significant effect on the performance of the cathode in a DMFC for current densities below 150 mA/cm². This effect has been quantified in three ways: cell electrical performance, apparent polarization, and true cathode polarization. It has been shown that cell voltages can be up to 50 mV higher when operating a DMFC at 0.5M vs. 1.0M, 60 °C methanol, 0.1 L/min ambient airflow, and at 100 mA/cm² applied load. When a cathode can be made to be sufficiently water rejecting, we once again see an increase in performance. At 60 °C, 0.5M methanol, 0.1L/min the fuel cell with the improved electrode structure could reach voltages as high as 0.449V. This is a 30 mV improvement over the previous design.

In summary, the performance of a Nafion-based DMFC is strongly impacted by the methanol crossover, especially at low airflow rates. The mass transfer limited condition of the cathode is considerably worsened by the methanol crossover. While one approach to solving this problem would be to use a membrane with lower methanol crossover, it has been demonstrated here that an improved cathode structure and operation at a lower methanol concentration will result in a significant enhancement of performance.

Acknowledgment

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